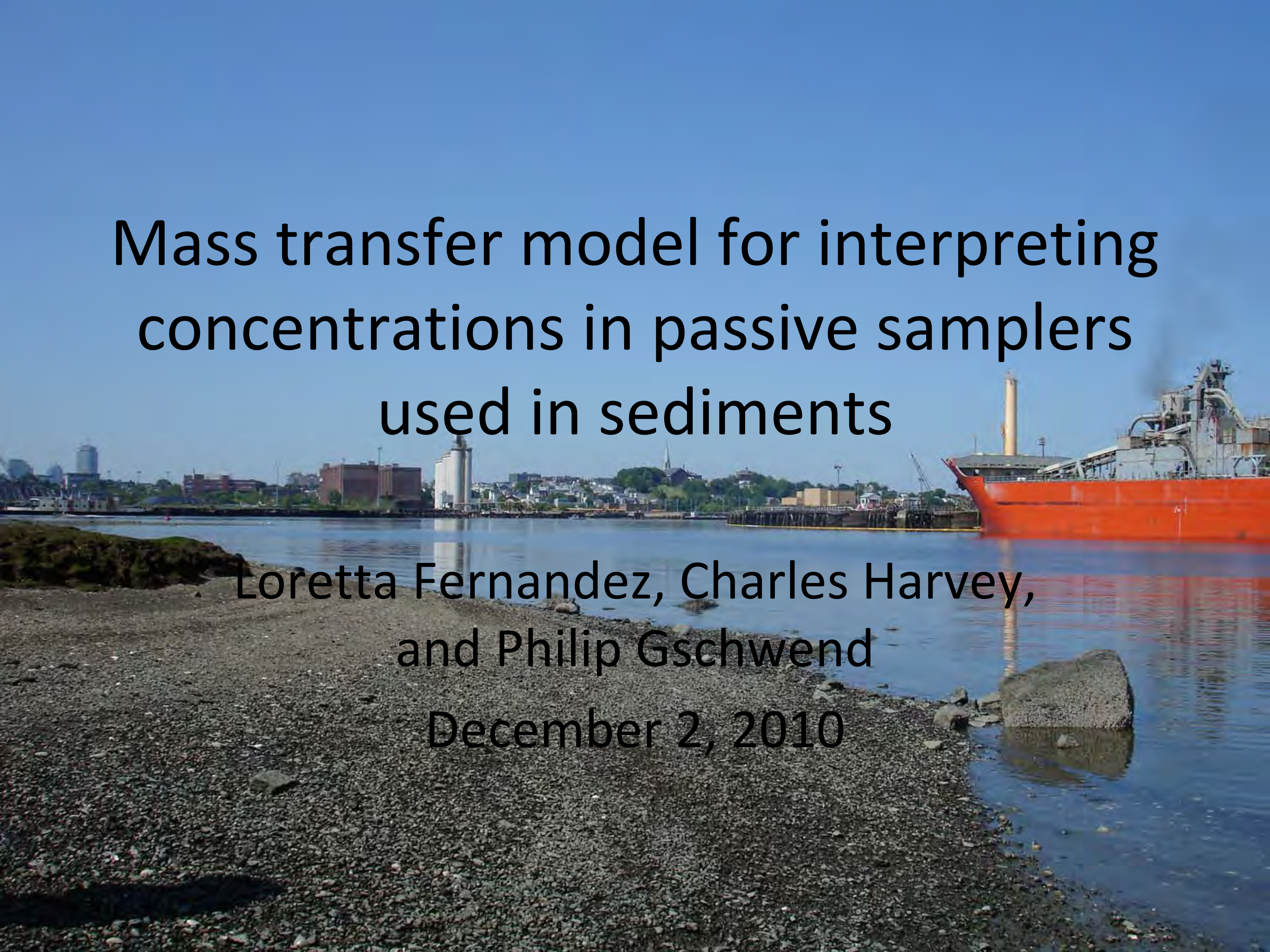

Mass transfer model for interpreting concentrations in passive samplers used in sediments

Loretta Fernandez, Charles Harvey, and Philip Gschwend

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14. ABSTRACT
Performance reference compounds (PRCs) are often used in passive sampling devices in order to allow sampler deployment for times shorter than would be required for full equilibration. They are especially important for in situ passive sampling of sediment beds, where equilibration of sampler and sediments could take years. In order to translate sampler concentration data, for both PRCs and target chemicals, into useful information such as water concentrations or chemical activities, an accurate mass-transfer model for the system is necessary. Here, a twophase diffusion model for a polymer sheet in porous media is described and its use demonstrated. A method for calibrating sampler/site-specific mass transfer behavior using three PRCs and the model is described. The accuracy of such results are compared to measured porewater concentrations of seventeen target polycyclic aromatic hydrocarbons in a test sediment. Finally the diffusion model is exercised to predict how air-filled pores would affect deployment times when using polyethylene to sample contaminants in soils.

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USING A DIFFUSIVE MASS TRANSFER MODEL TO INTERPRET CONTAMINANT UPTAKE BY POLYMERIC PASSIVE SAMPLERS FROM ENVIRONMENTAL POROUS MEDIA

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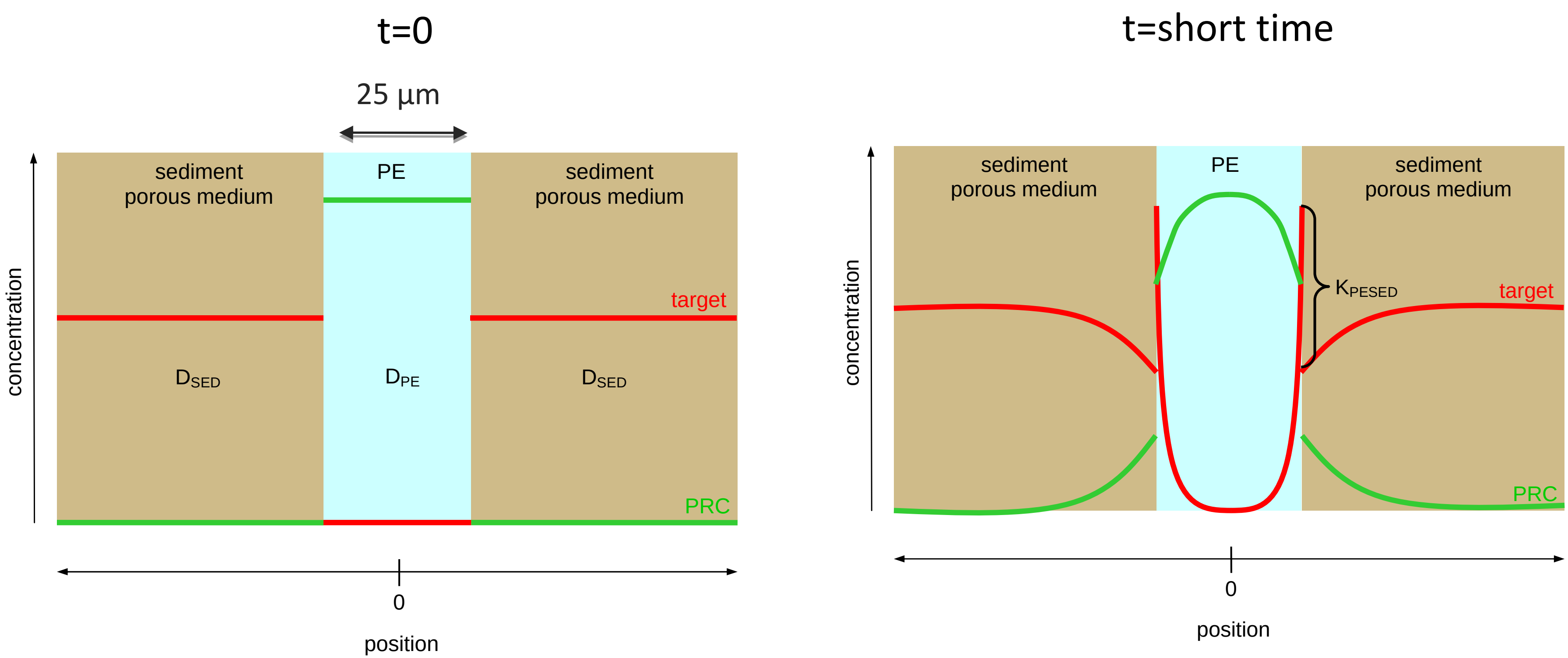
(Massachusetts Institute of Technology)

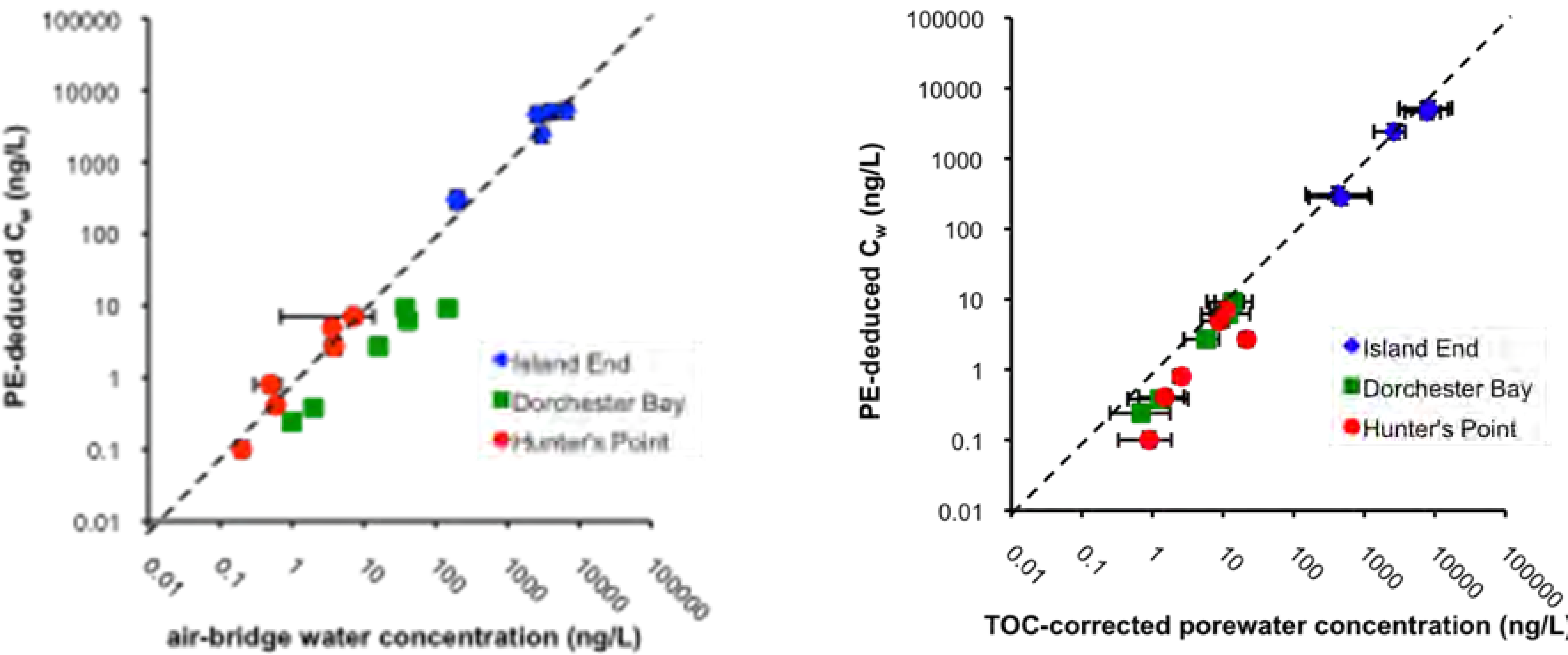
Performance reference compounds (PRCs) are often used in passive sampling devices in order to allow sampler deployment for times shorter than would be required for full equilibration. They are especially important for in situ passive sampling of sediment beds, where equilibration of sampler and sediments could take years. In order to translate sampler concentration data, for both PRCs and target chemicals, into useful information such as water concentrations or chemical activities, an accurate mass-transfer model for the system is necessary. Here, a two-phase diffusion model for a polymer sheet in porous media is described and its use demonstrated. A method for calibrating sampler/site-specific mass transfer behavior using three PRCs and the model is described. The accuracy of such results are compared to measured porewater concentrations of seventeen target polycyclic aromatic hydrocarbons in a test sediment. Finally, the diffusion model is exercised to predict how air-filled pores would affect deployment times when using polyethylene to sample contaminants in soils.

PE sampler in sediment



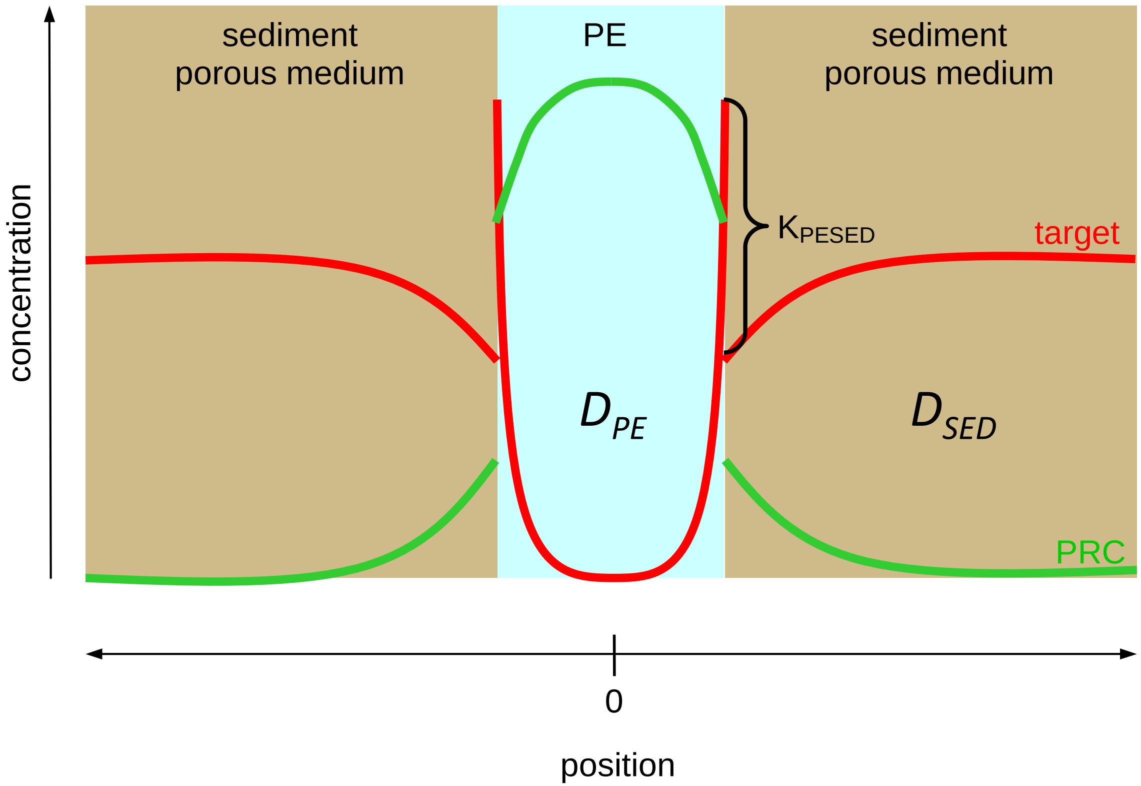
$$M_{target}(t) = k\,\frac{C^{o}_{targetSED}}{K_{SEDPE}}$$

$$M_{PRC}(t) = k\,C^{o}_{PRC,PE}$$



PE-deduced C_w (ng/L)
100000
10000
1000
100
10
1
0.1
0.01
0.01
0.1
1
10
100
1000
10000
100000
air-bridge water concentration (ng/L)
Island End
Dorchester Bay
Hunter's Point
PE-deduced C_w (ng/L)
TOC-corrected porewater concentration (ng/L)

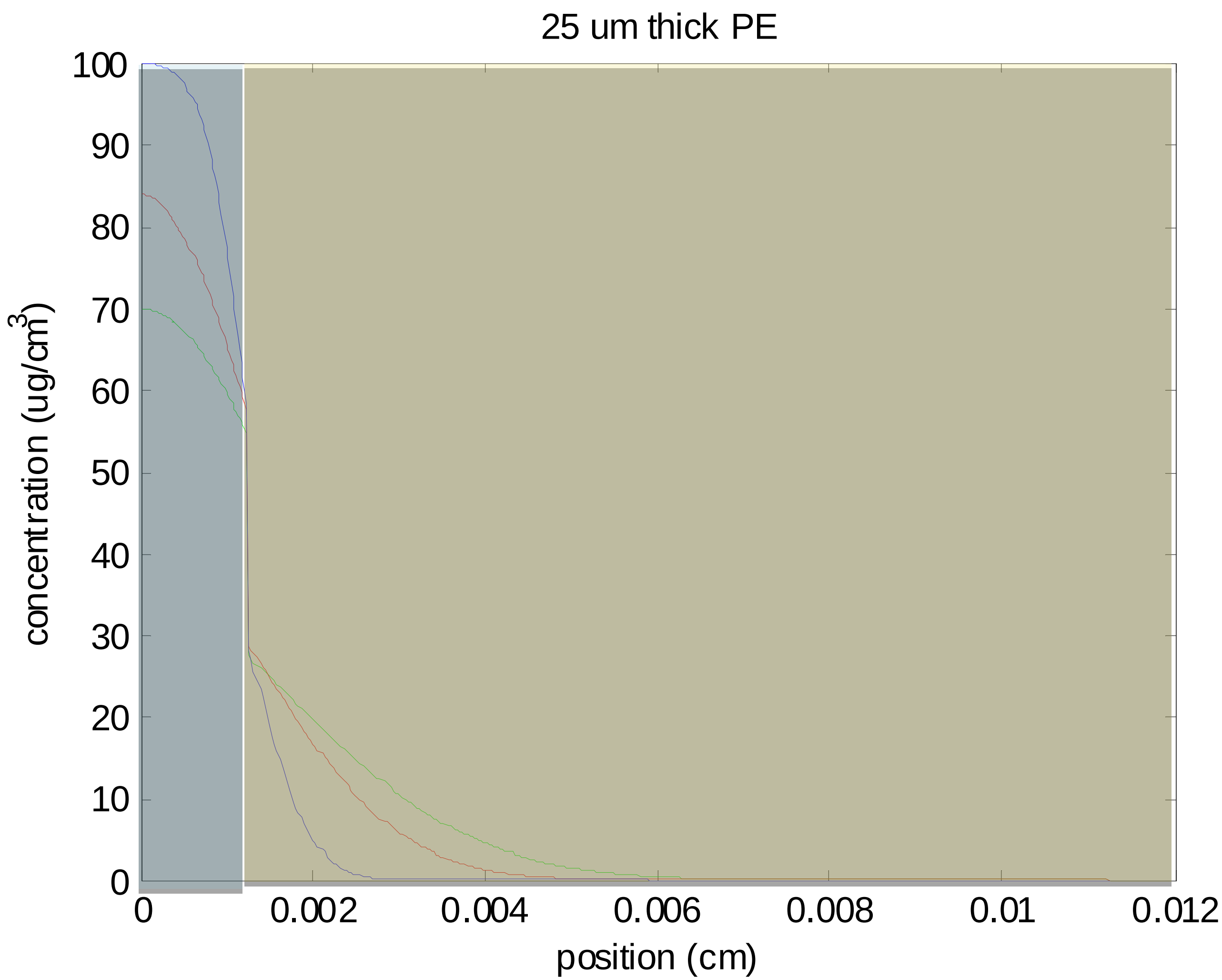
PE sampler in sediment



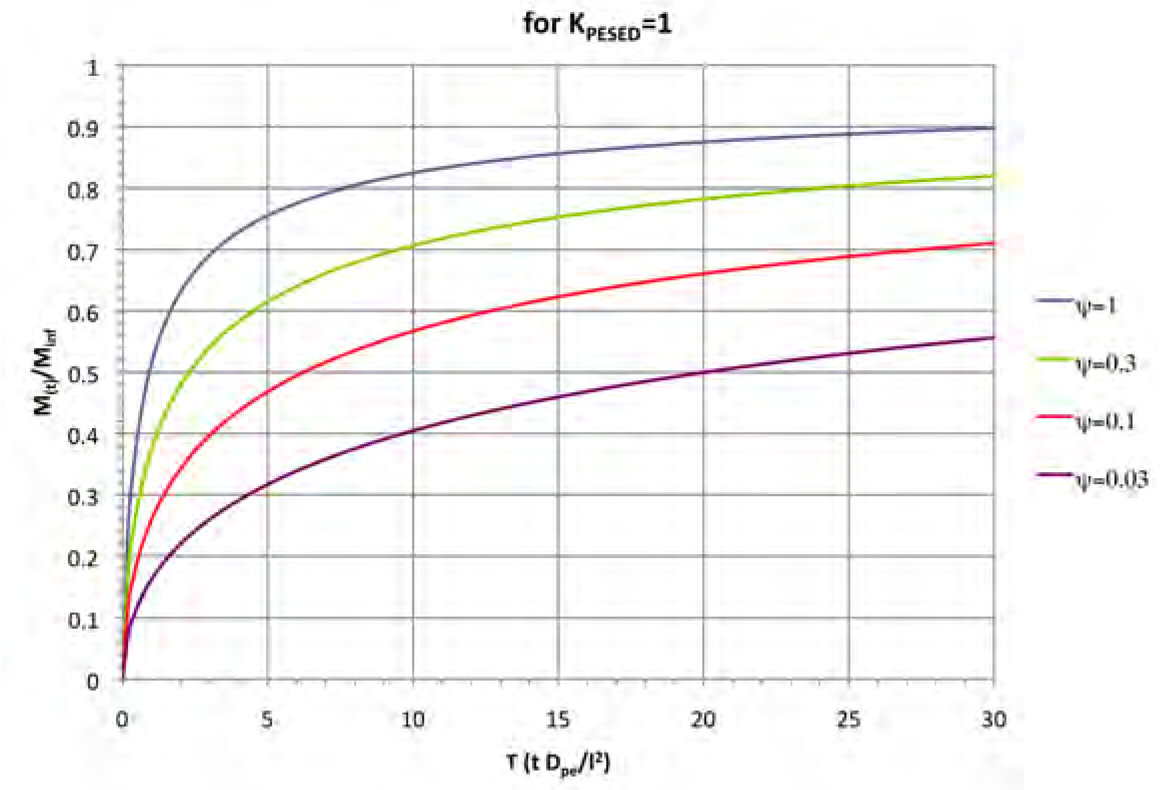
$$D_{SED} = \frac{D_W}{(1 + r_{sw} K_d)\,\tau}$$

$$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \qquad \frac{\partial C_{SED}}{\partial t} = D_{SED} \frac{\partial^2 C_{SED}}{\partial x^2}$$

Numerical model of mass transfer



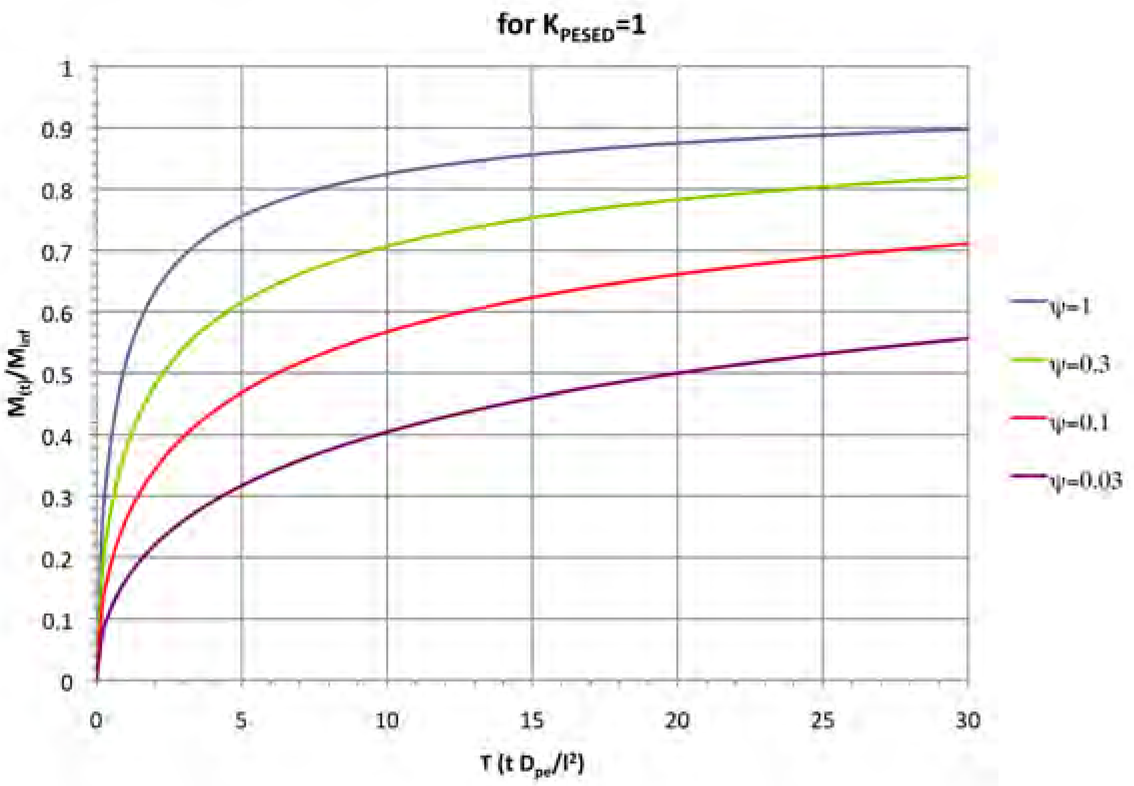
Laplace space solution to mass-transfer model



$$\psi = \frac{D_{SED}}{D_{PE}} = \frac{D_W}{(1 + r_{sw} K_d)\,\tau\, D_{PE}} \approx \frac{D_W}{r_{sw} K_d\, \tau\, D_{PE}}$$

$$K_{PESED} = \frac{K_{PEW}}{K_d}$$

Laplace space solution to mass-transfer model



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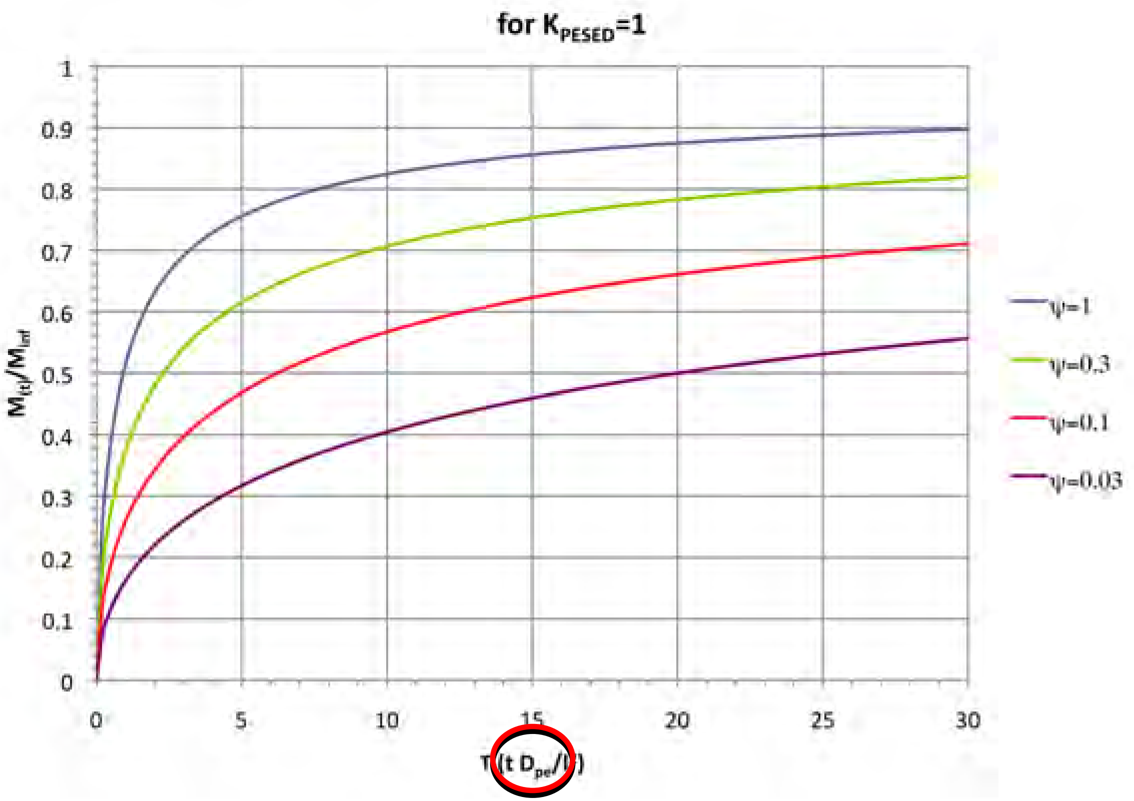
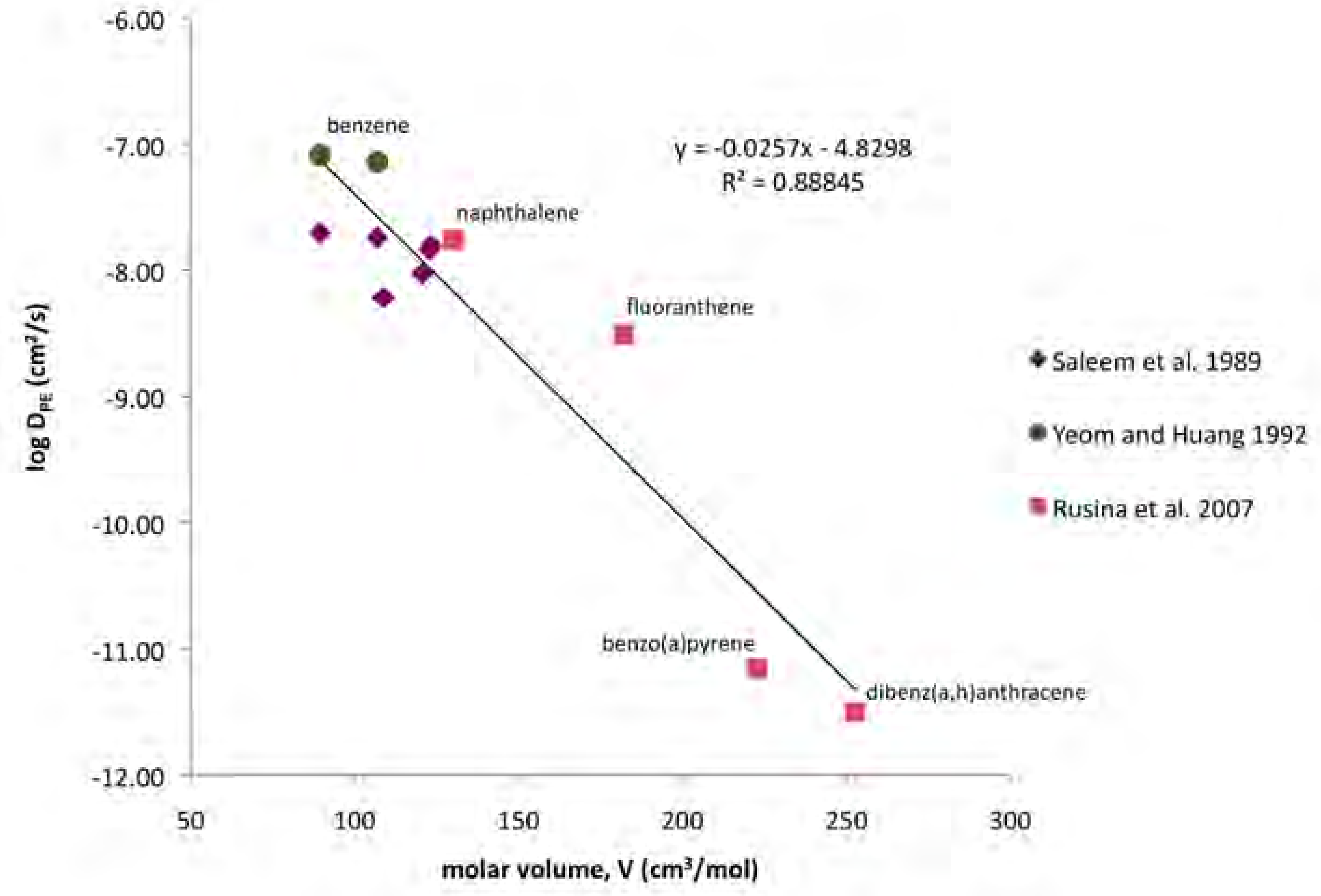


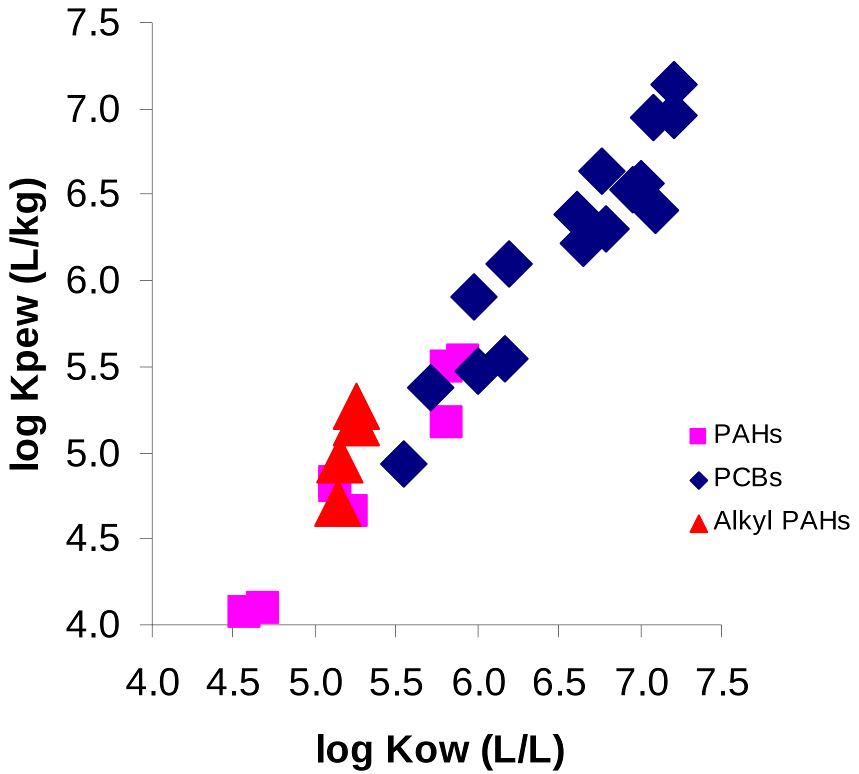
$$\psi = \frac{D_{SED}}{D_{PE}} = \frac{D_W}{(1 + r_{sw} K_d)\, \tau\, D_{PE}} \approx \frac{D_W}{r_{sw} K_d\ \tau\, D_{PE}}$$

$$K_{PESED} = \frac{K_{PEW}}{K_d}$$

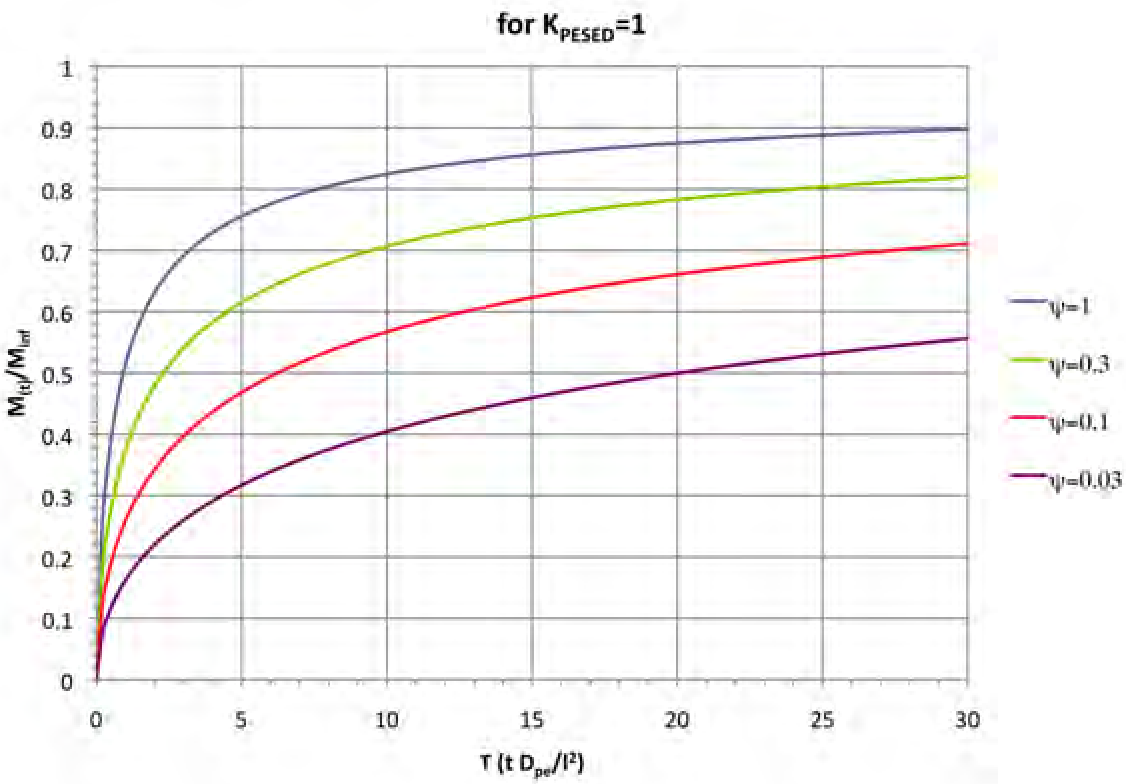
Relationship between log D_{PE} and molar volume



Relationship between log K_{PEW} and log K_{OW}



Laplace space solution to mass-transfer model

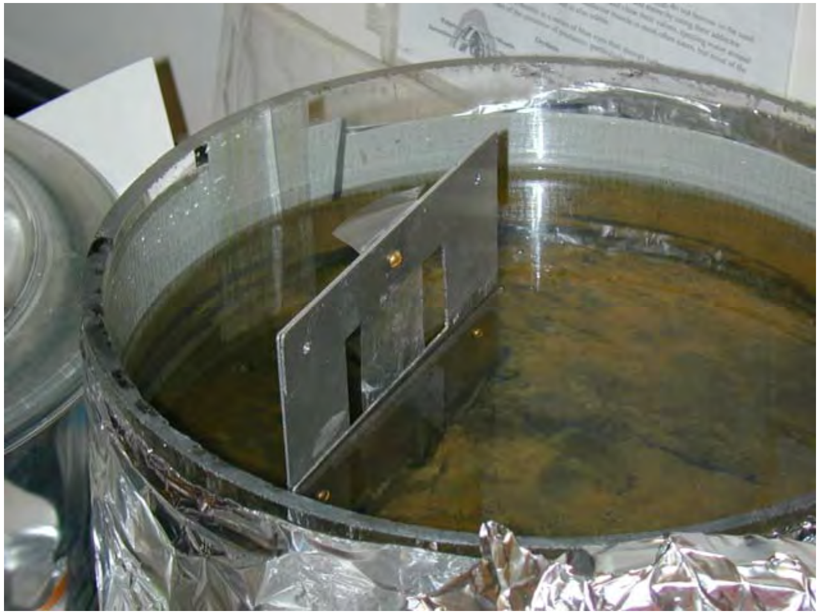


$$\psi = \frac{D_{SED}}{D_{PE}} = \frac{D_W}{(1 + r_{sw} K_d)\, \tau D_{PE}} \approx \frac{D_W}{r_{sw} K_d\ \tau D_{PE}}$$

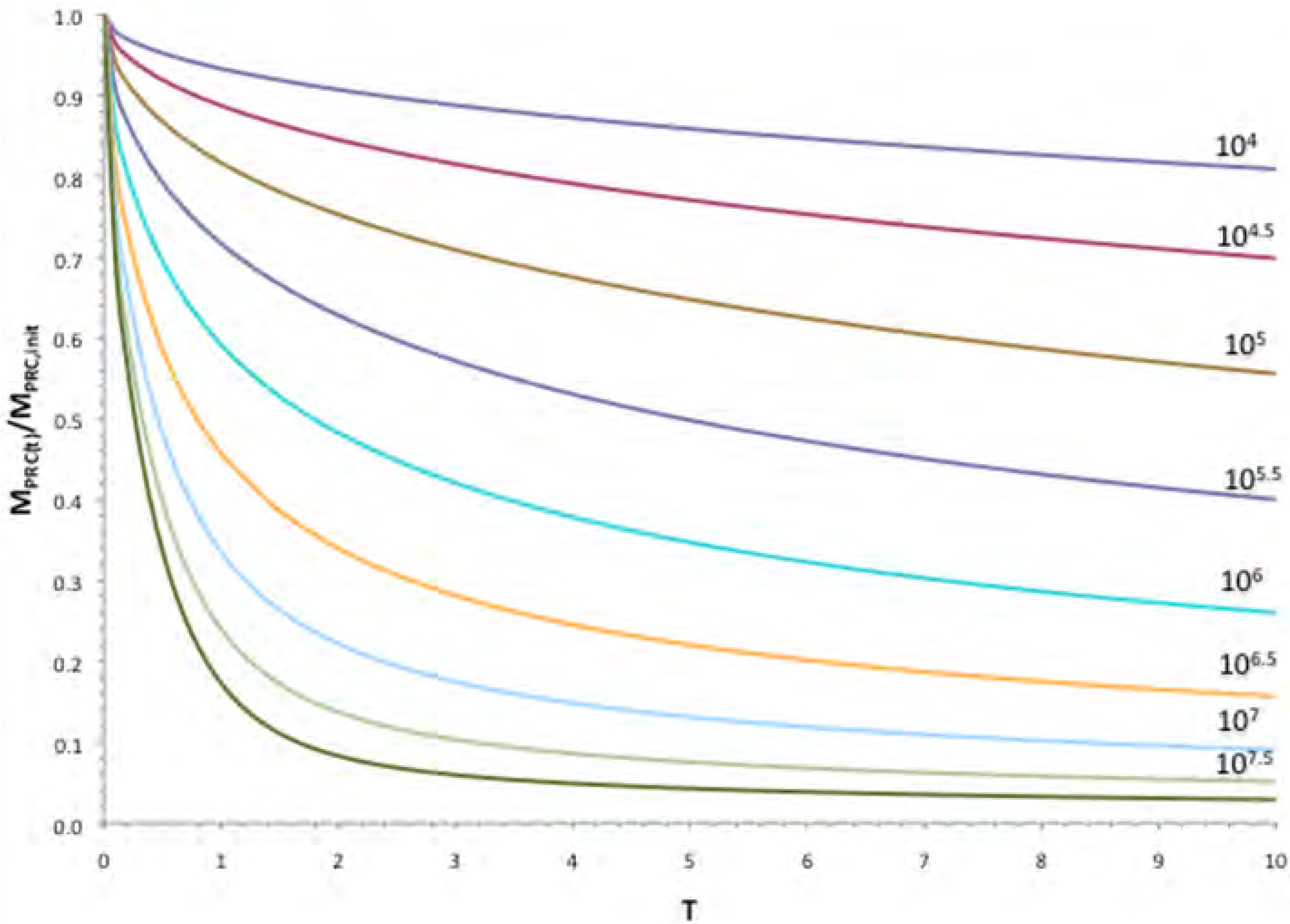
$$K_{PESED} = \frac{K_{PEW}}{K_d}$$

sediment collection

homogenized sediments



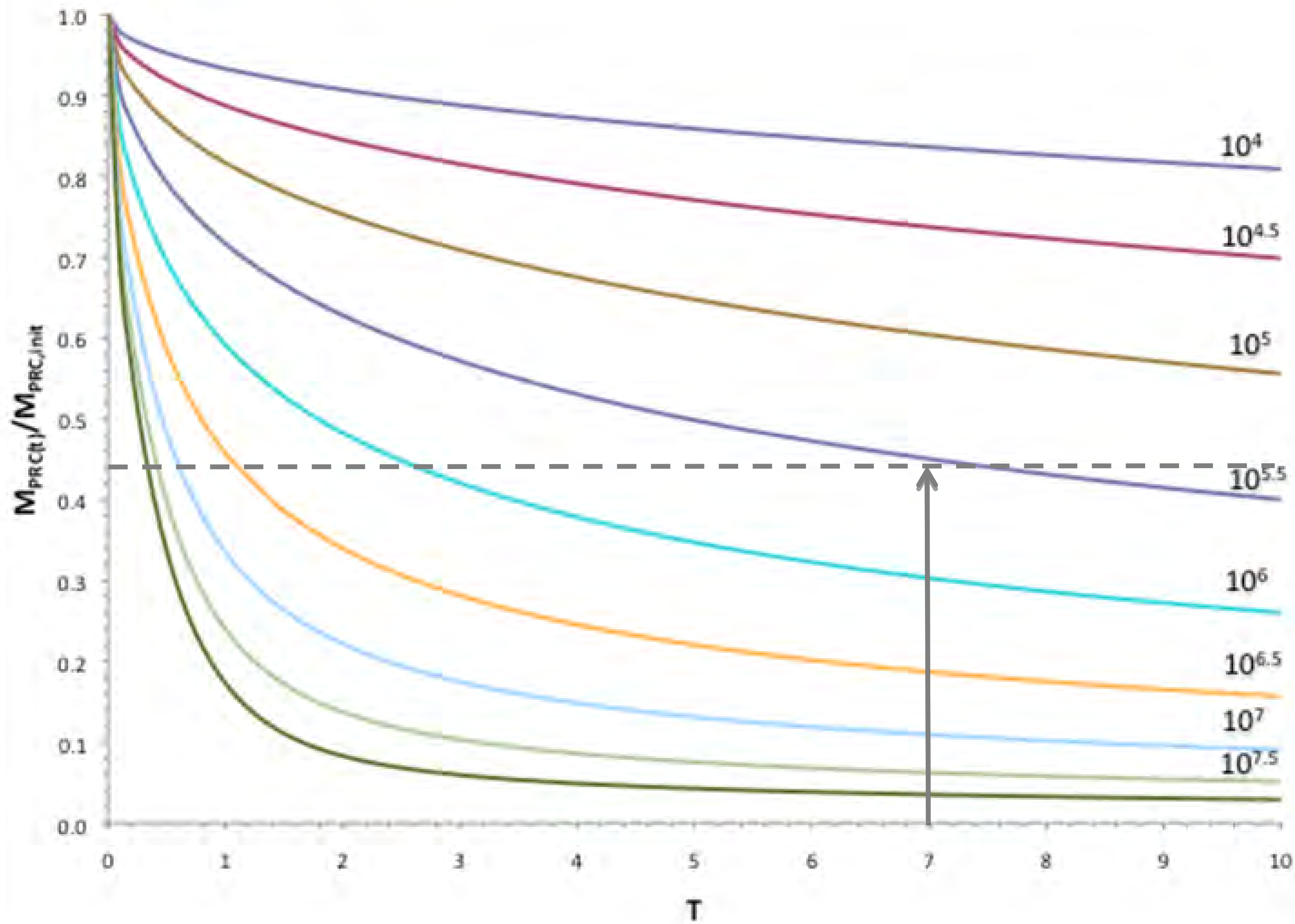
d12-chrysene



51 µm PE
10 day exposure ; T=7

25 µm PE
3 day exposure ; T=8.5

d12-chrysene



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10 day exposure ; T=7

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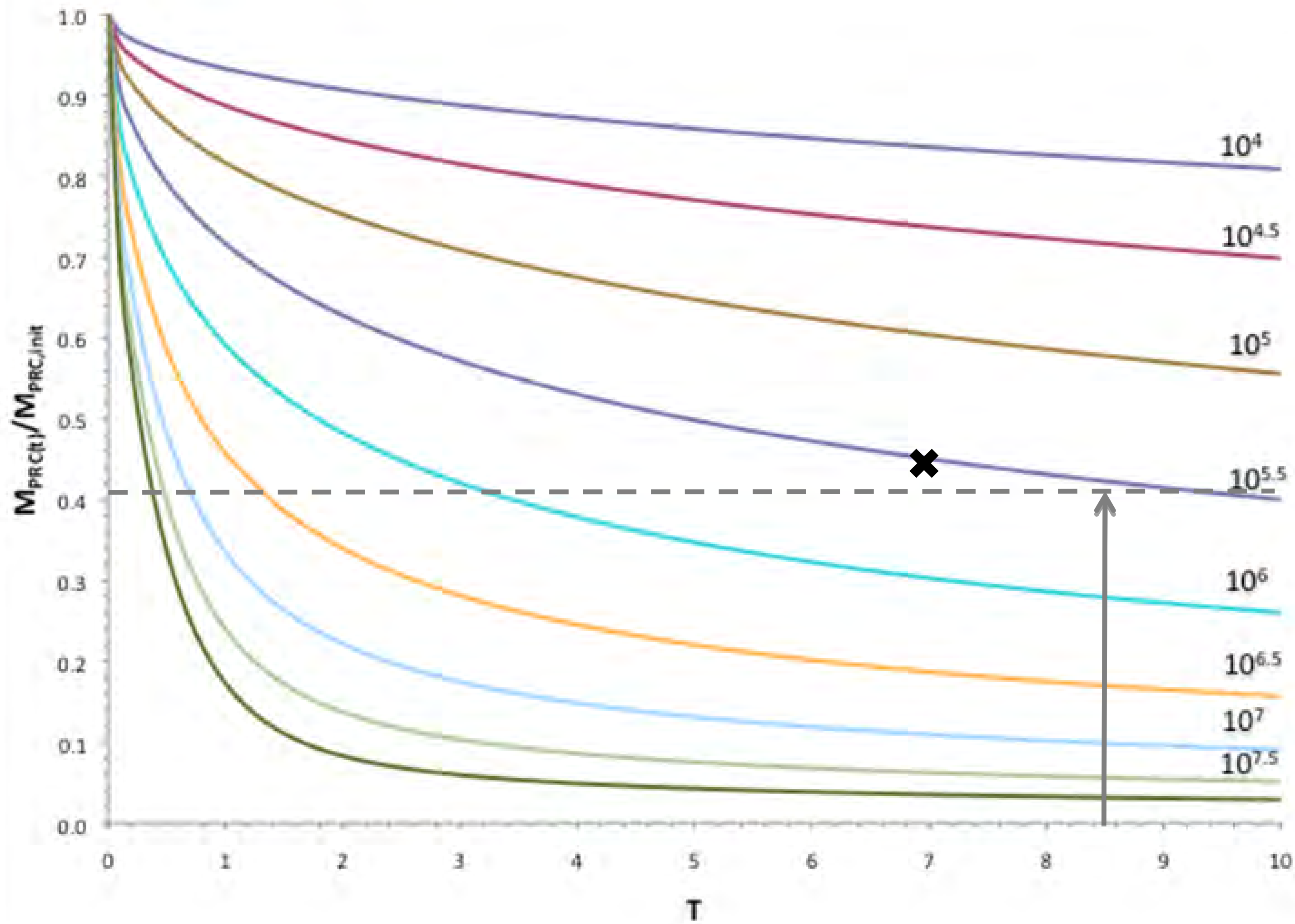

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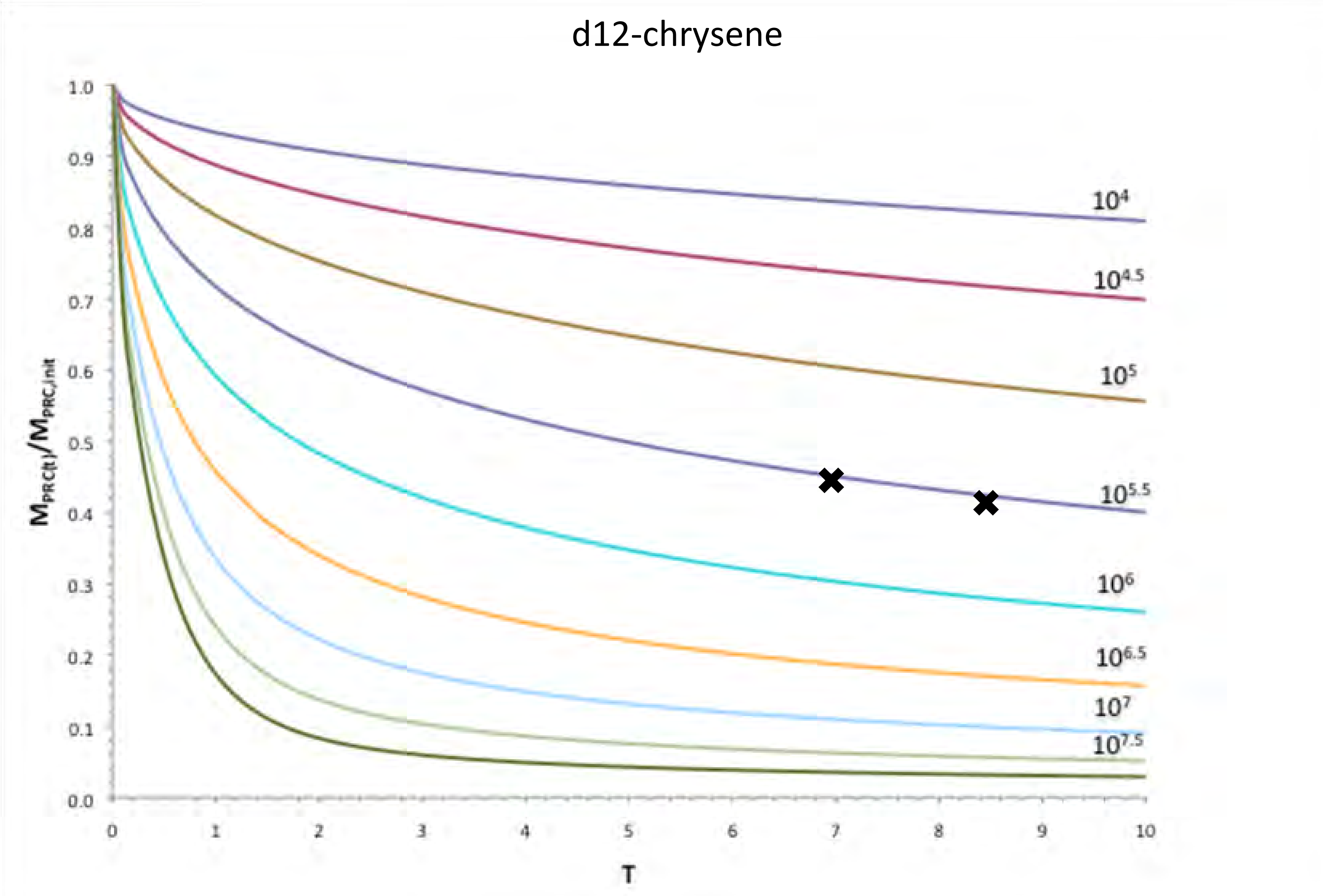
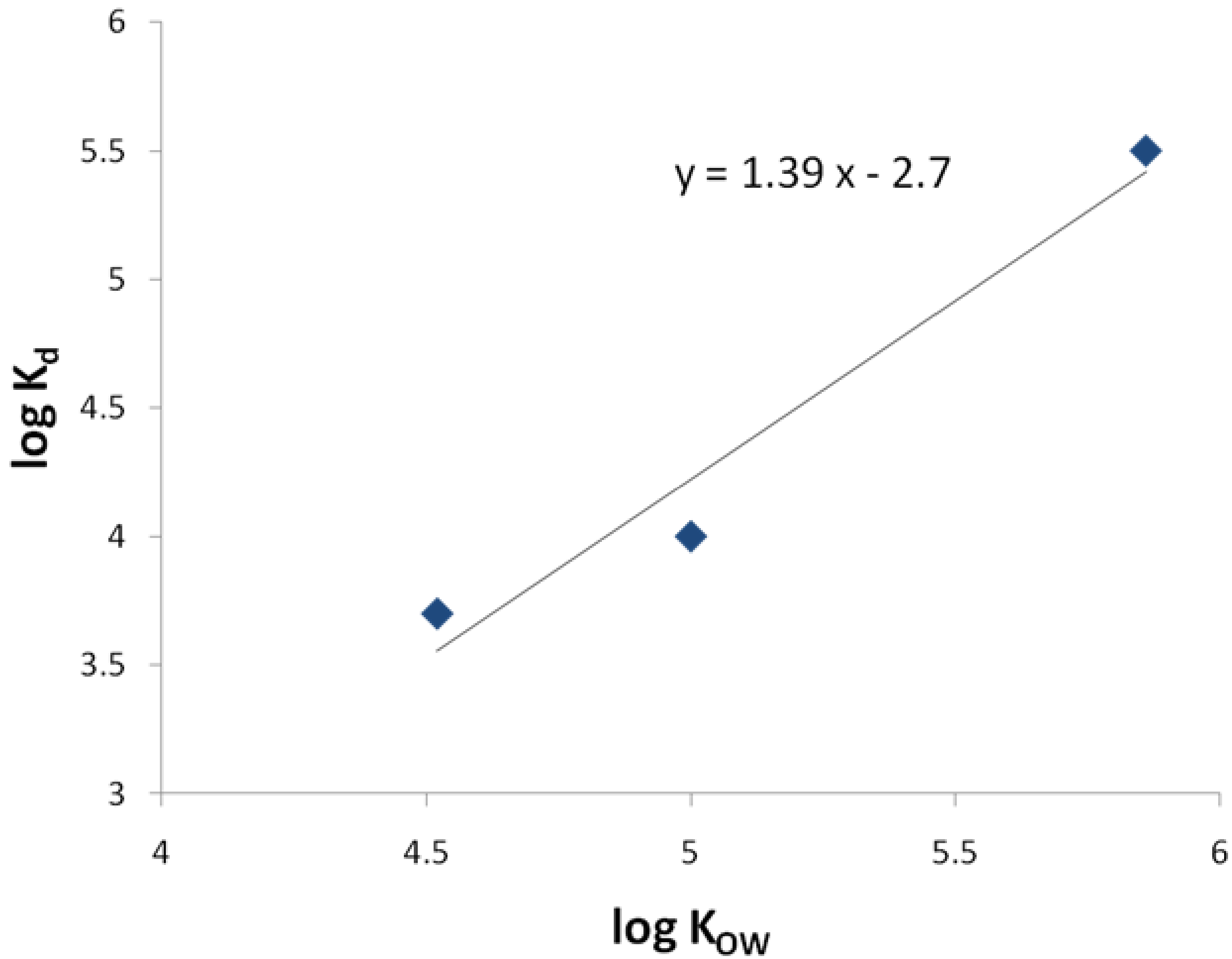


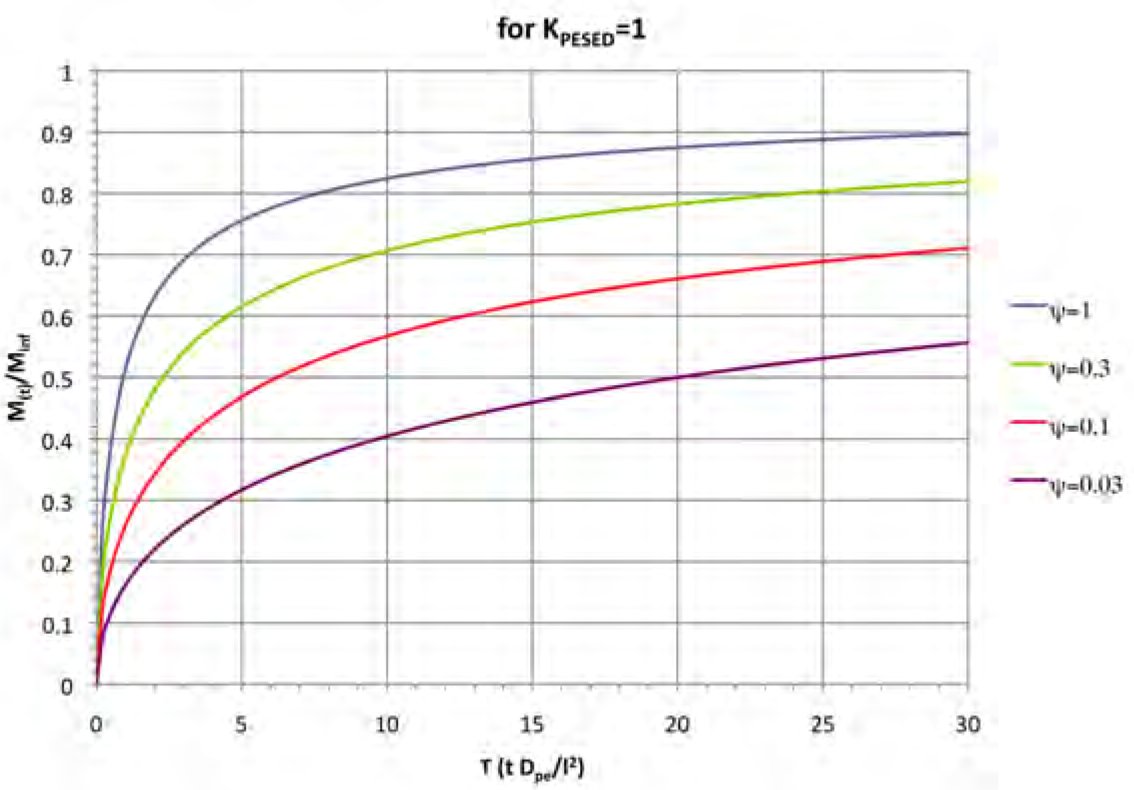
51 µm PE
10 day exposure ; T=7

25 µm PE
3 day exposure ; T=8.5

Use PRCs to find relationship between log K_d and log K_{OW}



Laplace space solution to mass-transfer model



$$\psi = \frac{D_{SED}}{D_{PE}} = \frac{D_W}{(1 + r_{sw} K_d)\,\tau\, D_{PE}} \approx \frac{D_W}{r_{sw} K_d\, \tau\, D_{PE}}$$

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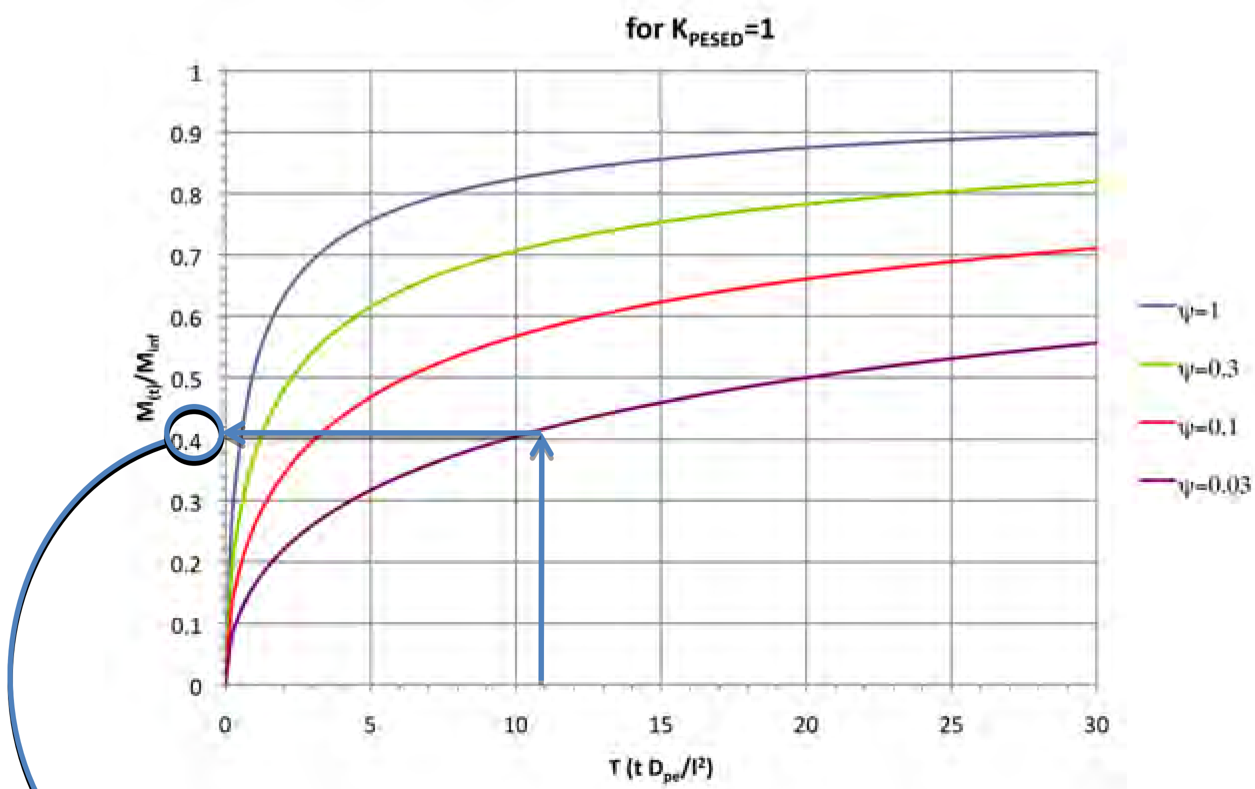
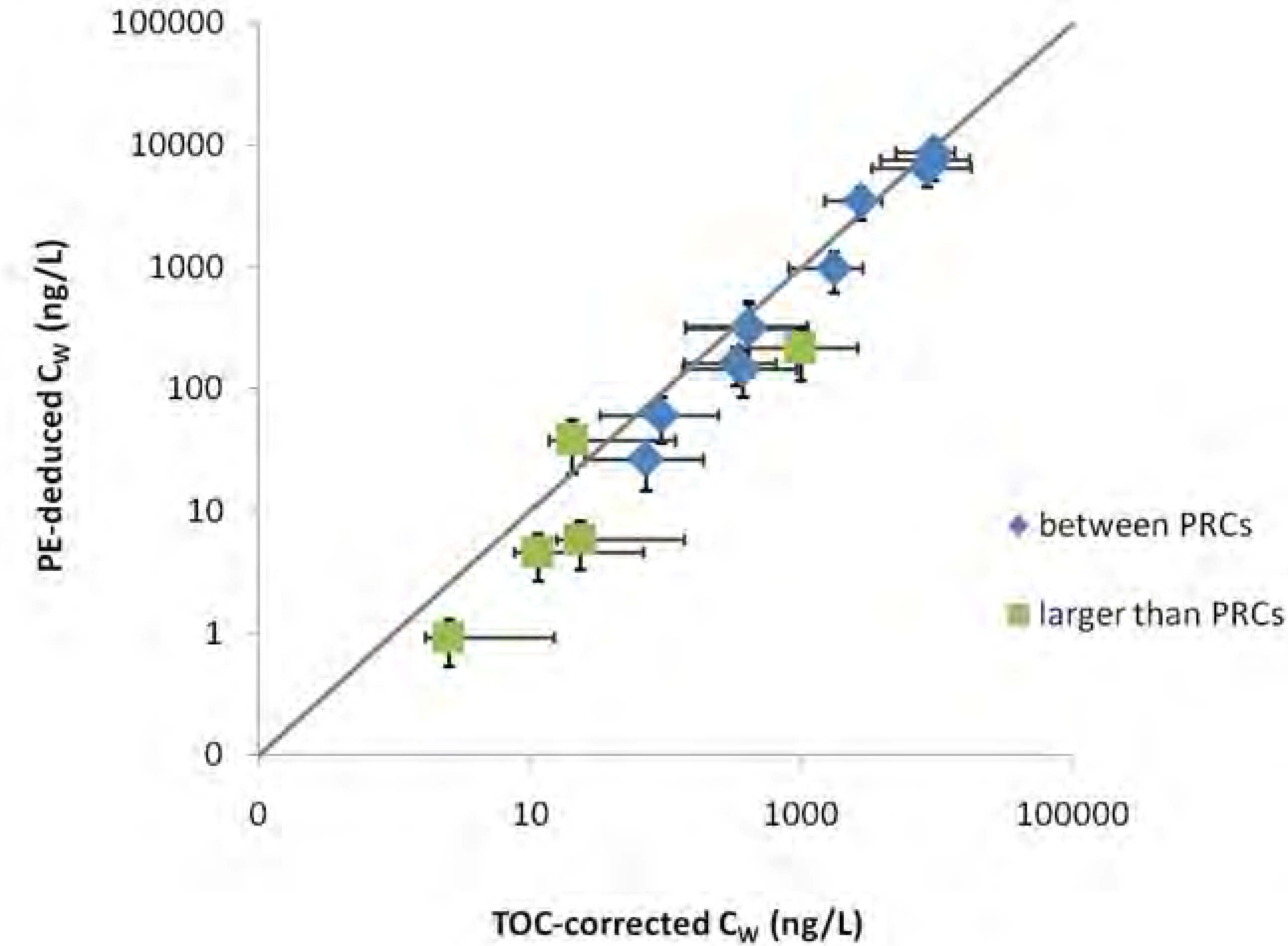


$$\frac{M_{in\,PE}(t)}{fraction\ to\ equilibrium} = M_{in\,PE}\ at\ equilibrium$$

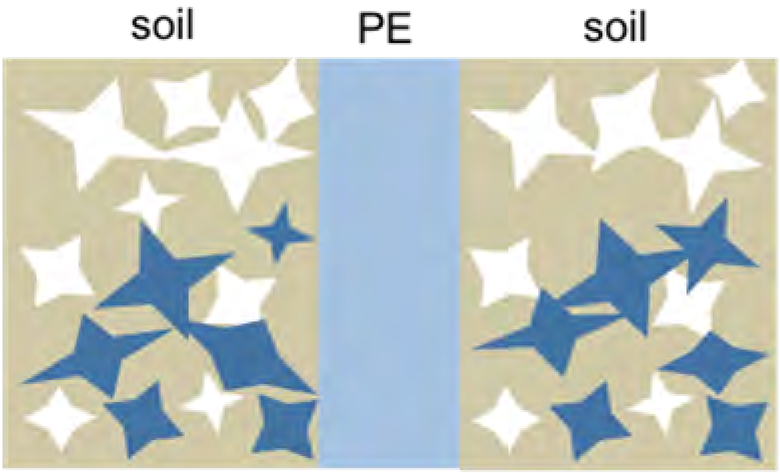
$$\frac{M_{PE}\ at\ equilibrium}{Mass\ of\ sampler} = C_{PE}\ at\ equilibrium$$

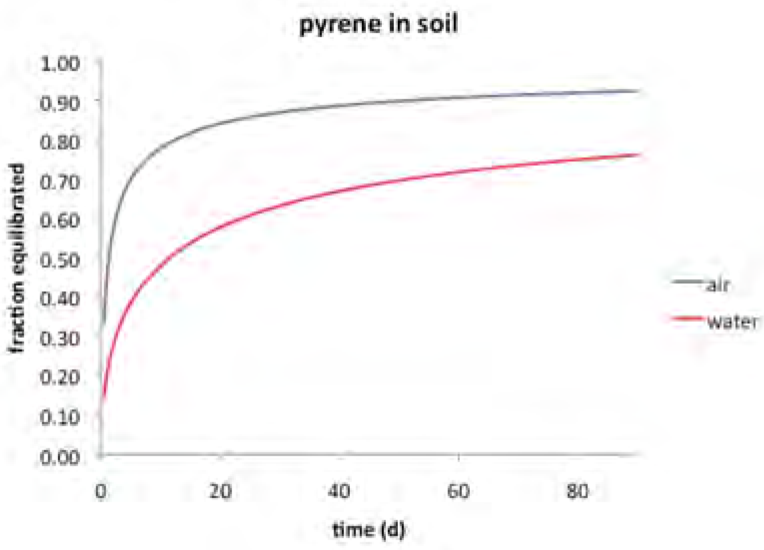
$\Rightarrow$ C_W or a

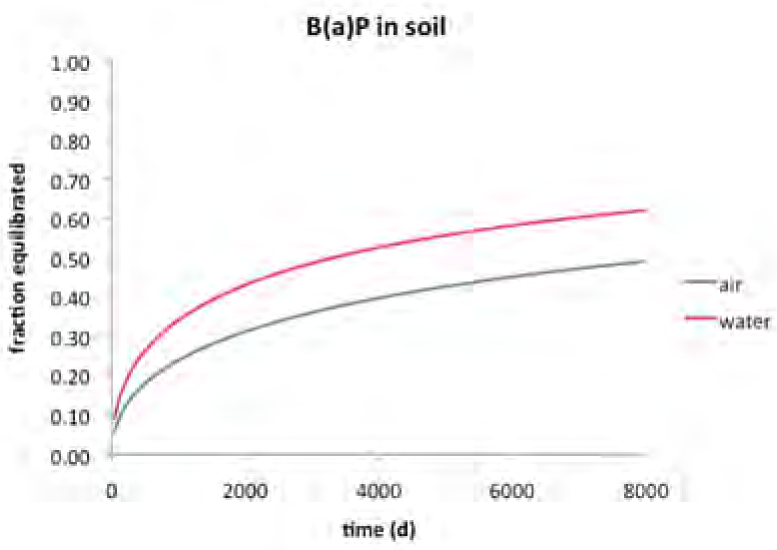


100000
10000
1000
100
10
1
0
0
10
1000
100000
PE-deduced C_W (ng/L)
TOC-corrected C_W (ng/L)
between PRCs
larger than PRCs

mass transfer model for polymer in soils

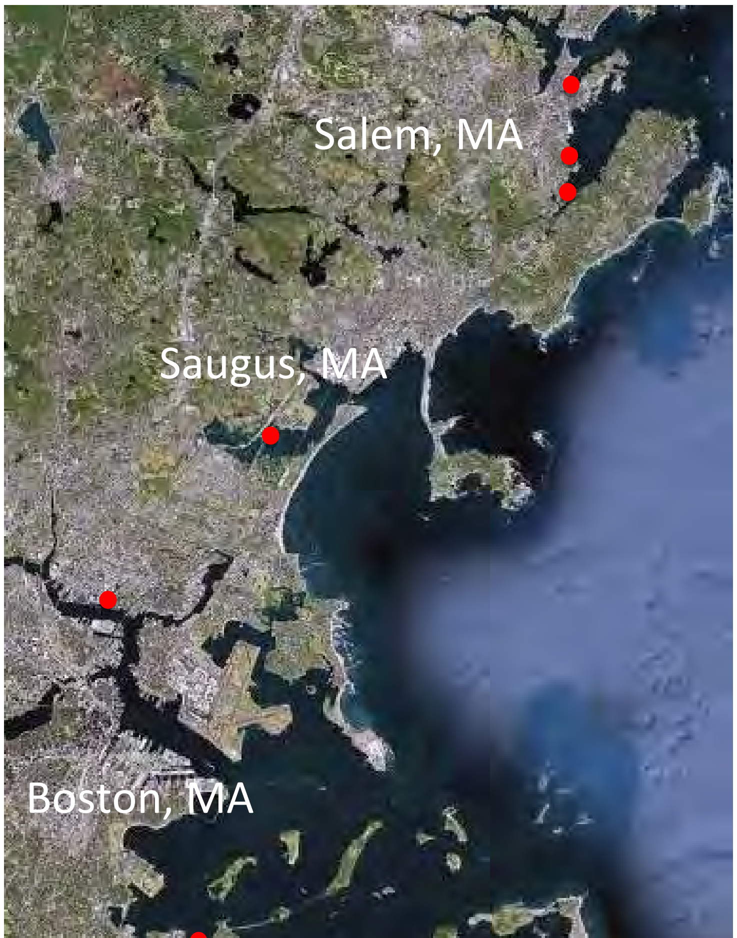


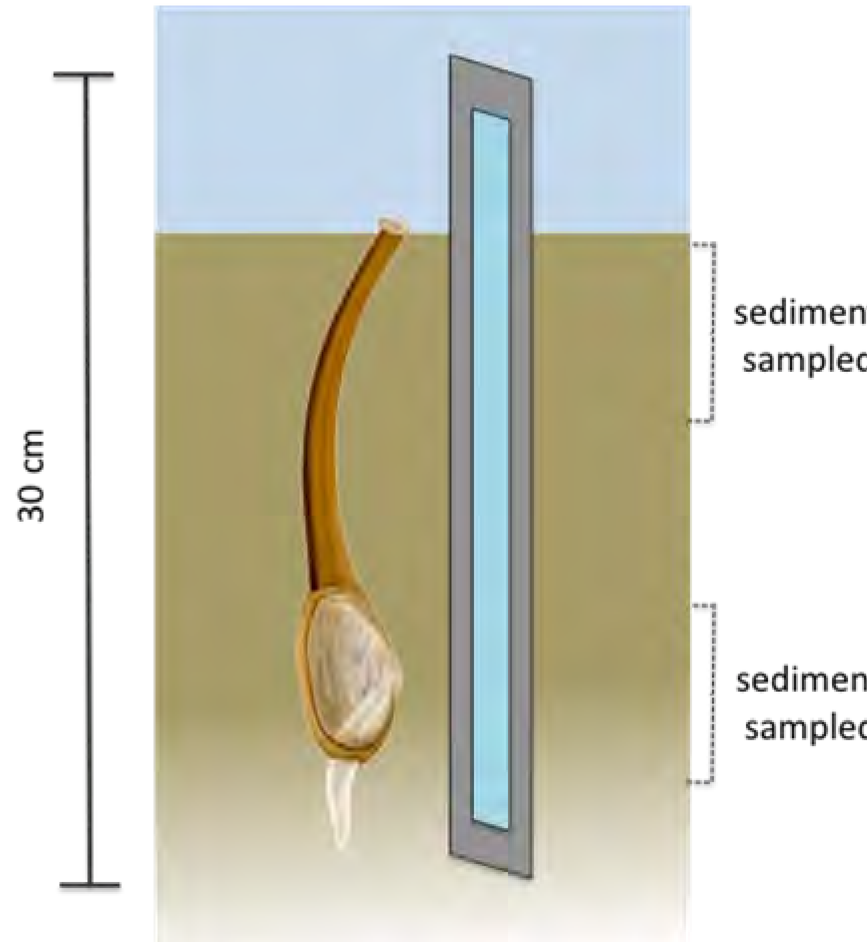


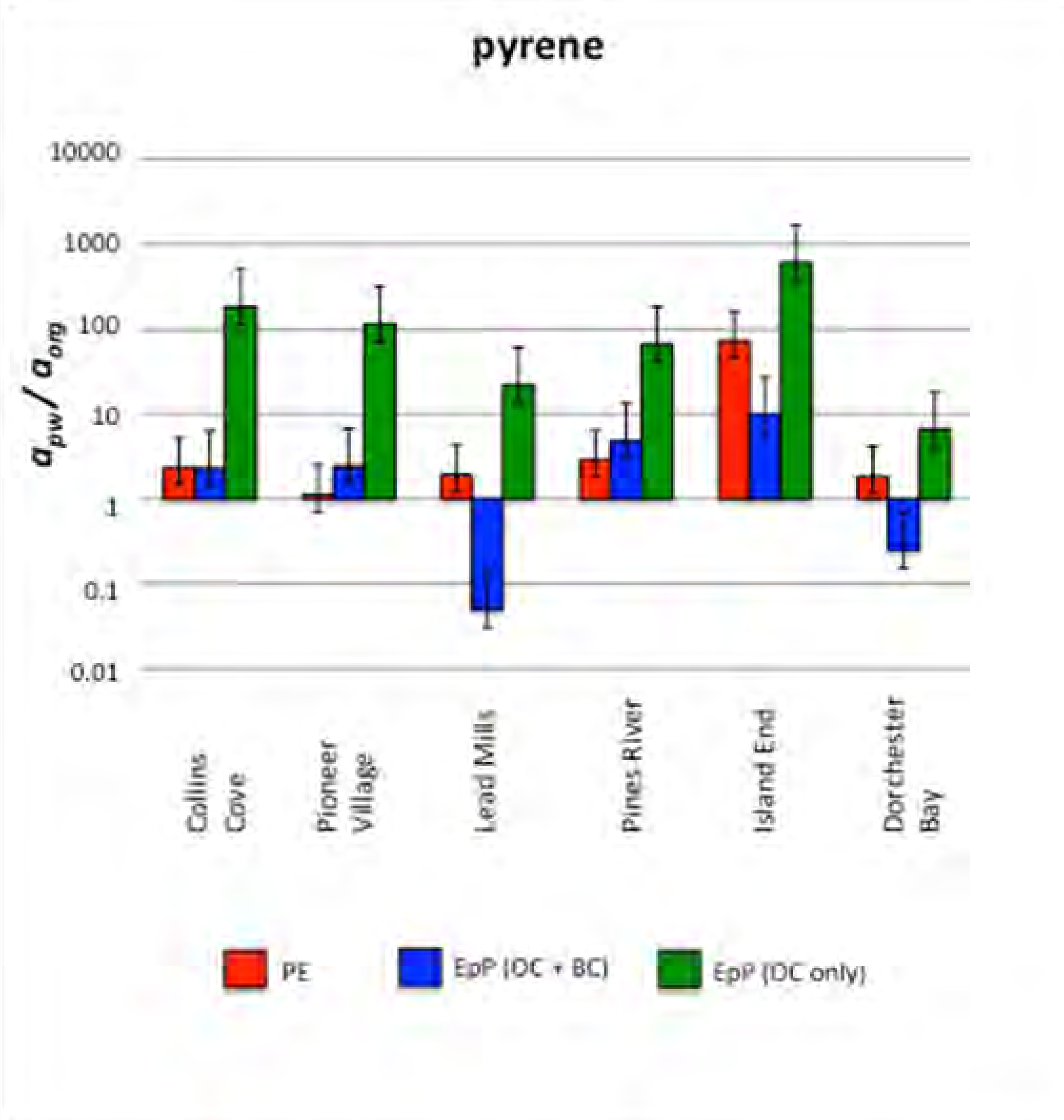


Can we measure C_w or a directly in porewaters and do they correlate with organism concentrations?

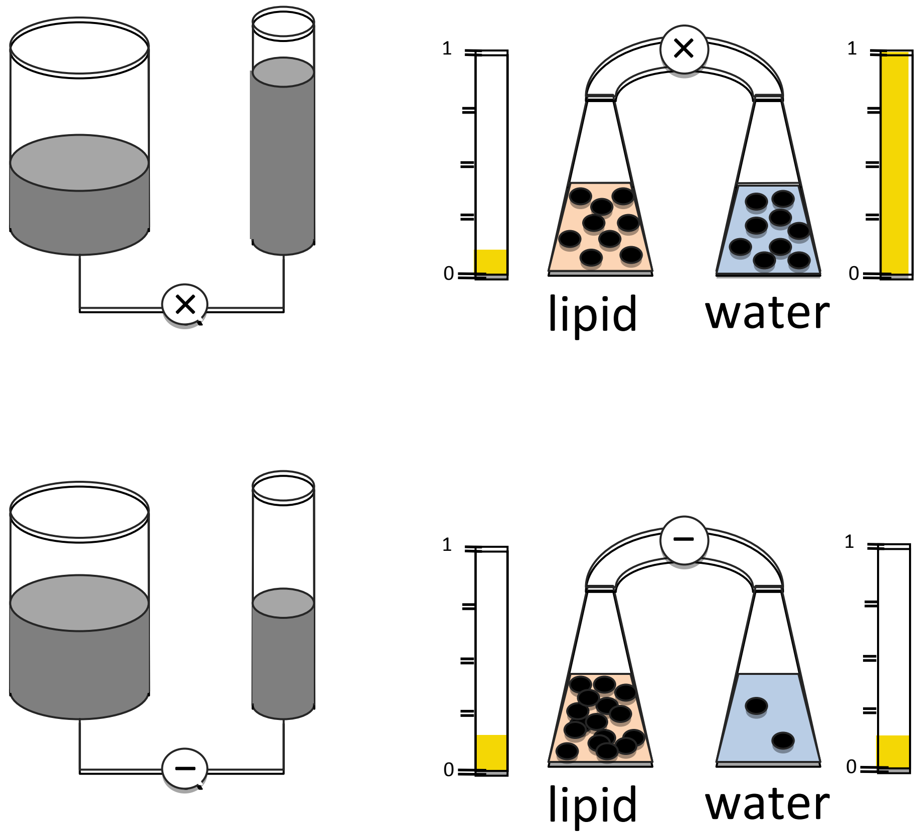
"availability" → a or C_w






pyrene
a_{pw}/a_{org}
10000
1000
100
10
1
0.1
0.01
Collins Cove
Pioneer Village
Lead Mills
Pines River
Island End
Dorchester Bay
PE
EpP (OC + BC)
EpP (OC only)

HOC chemical activity (fugacity) in sediments



$$a_{phase} = \frac{(C_{phase} / K_{phase-w})}{C_w^{sat}(L)}$$

reference concentration

$$C_w = a \; C_w^{sat}(L)$$

(modified from Schwarzenbach, Gschwend, and Imboden 2002)